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Glass Reinforced-Diallylbisphenol / Maleimide Composites with Modified Interphases

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Abstract

A silane coupling agent, based on the reaction between γ -aminopropyltriethoxysilane (APS) and maleic anhydride (MA), was prepared. The coupling agent, maleamidopropylsilane (MAPS), was chemisorbed onto E-glass cloth. TGA analysis of the treated glass cloth showed 0.8% weight loss (silane loading), when heated to 700 °C in an air atmosphere. The treated glass cloths were used in the fabrication of composite laminates having approximately 60 \pm 1 wt% glass reinforcement, with the matrix being a thermosetting system based on diallylbisphenol (DAP) / bismaleimide (BMI). DMTA analysis of the cured composite laminates showed unexpected 10-20 GPa increase in the modulus and a 30-40 °C increase in the T_g for the treated versus untreated glass cloths.

Background

Plueddemann demonstrated that glass reinforcements modified with silane coupling agents possessing a terminal reactive group gave composites having better properties than those made with reinforcements modified with coupling agents with unreactive terminal groups.¹ An interphase of approximately 5 to 100 Å in thickness is required for optimal properties. Although the attainment of a perfect surface coverage of glass is improbable, factors influencing the deposition of silanes with roughly appropriate thicknesses include pH, water content, temperature and silane concentration. Deposition of silanes onto glass surfaces can only occur through the hydrolyzed silane form. The conditions needed for alkoxysilane hydrolysis also facilitate condensation of the siloxanes thus precautions are needed to reduce the degree of condensation.

Dissipation and transfer of energy at the interphase is essential in order for composites to attain optimal properties. The interphase is the region between the ductile matrix and the stronger but more brittle fibers. Blum investigated BMI model composite systems made from silica gel that were treated with APS.² The terminal amino group of the adsorbed coupling agent was then reacted (Michael addition) with the maleimide group of BMI. ¹³C NMR (CP/MAS) of the model composites revealed fast relaxation times. Fast relaxation times are indicative of

internal energy dissipation modes at the interphase, or the ability of the interphase to transfer the energy effectively.

In composites systems, heating and cooling cycles are necessary for processing and composite fabrication. Stresses are built up at the interphase region from shrinkage of the matrix during crosslinking. Additional stresses are incurred due to mismatches of the coefficients of thermal expansions of the fiber and matrix. Further mismatch in the moduli and elastic properties of the fiber and matrix, respectively, also add to the problem. Interphases that can accommodate the volume shrinkage and stress mismatches, while maintaining a covalent bond between the matrix and reinforcement would be ideal.

Experimentals. Results and Discussion

The coupling agent was prepared by the stoichiometric addition of APS to MA under stringently dry and inert conditions. The maleamide coupling agent (MAPS) was obtained in good yields. Attempts to cyclize MAPS to the maleimide were unsuccessful. Conditions for cyclization involve heat and/or the presence of acidic species. Such conditions combined with the liberation of water from imidization-cyclodehydration lead to hydrolysis of the alkoxysilane groups causing subsequent condensation to the siloxane. This condensed species is inappropriate for use as a coupling agent since it would give an interphase with more than optimum thickness. The synthesis of MAPS is shown in Figure 1. The ^{13}C NMR spectra of precursors and MAPS are shown in Figure 2.

Glass treatment was accomplished by first heating glass cloth under vacuum for 24 hours. An acetone/water (90/10) deposition solution was prepared and acidified to pH 3. MAPS (2%) was added to the deposition solution the glass cloth subsequently immersed to effect treatment. The glass cloths were then heated at 116 °C under vacuum for 16 hours to complete chemisorption. TGA analysis of the glass cloth showed loading levels of 0.8%, as shown in Figure 3.

Diallylbisphenol A and bismaleimide were oligomerized to give the prepolymer used in composite fabrication. This oligomer has the appropriate properties, from viscosity and molecular weight perspectives, necessary for impregnation and thermal stability for the initial crosslinking heat/cure schedule. The prepolymer used in impregnation of the glass cloths was prepared by heating the two monomers at 125 °C for 30 mins under nitrogen atmosphere. Consolidation and initial cure were obtained under vacuum bagging conditions. Curing involved heating at 185 °C and 200 °C for 1 hour each, followed by postcuring at 250 °C for 6 hours.

DMTA analysis (Polymer Laboratories Mk III) of the laminates using a double cantilever head and a frequency of 10 hertz to 350 °C showed approximately 10 to 20 GPa increase in modulus, and a 30 to 40 °C increase in T_g for the treated glass versus the untreated glass composites. Figure 4 shows the DMTA plot.

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Conclusions

A coupling agent was made from the condensation of APS and MA. The coupling agent was immobilized onto glass cloth reinforcement. Loading levels of approximately 0.8% were obtained. Composites were fabricated using glass cloths that were treated with MAPS using untreated glass cloths as the controls. The composites showed a 10 to 20 GPa increase in the modulus and a 30 to 40 °C increase in the T_g. Further evaluations of these systems are ongoing, results will be presented.

References

1. Plueddemann, E. P. *Silane Coupling Agents*, 2nd Ed. Plenum Press: 1992, New York.
2. Gamboni, J. E.; Blum, F. D. *Macromolecules*, 1992, 4526-4534.

Figures

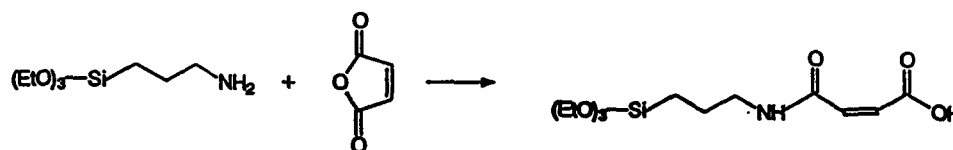


Figure 1. Synthesis of Maleamidopropyltriethoxysilane (MAPS).

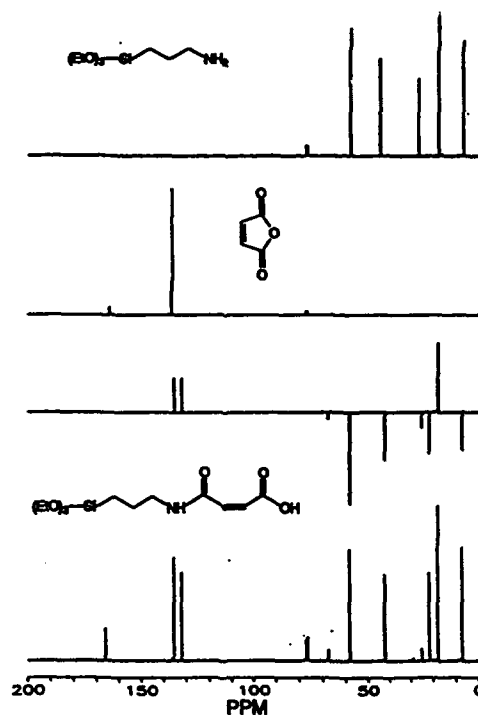


Figure 2. ¹³C NMR of APS (top), MA (upper-middle) and MAPS (bottom), (lower-middle shows the DEPT 135 spectrum).

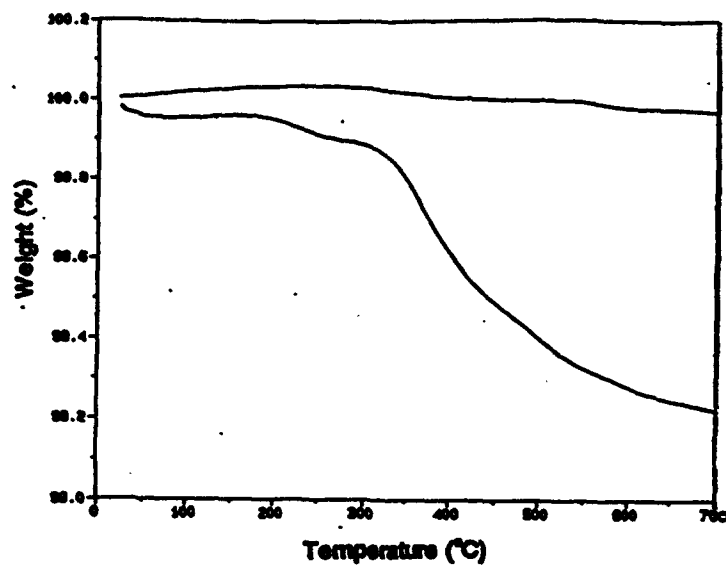


Figure 3. TGA analysis of untreated glass cloth (top) and Maleimidepropylsilane treated glass cloth (bottom).

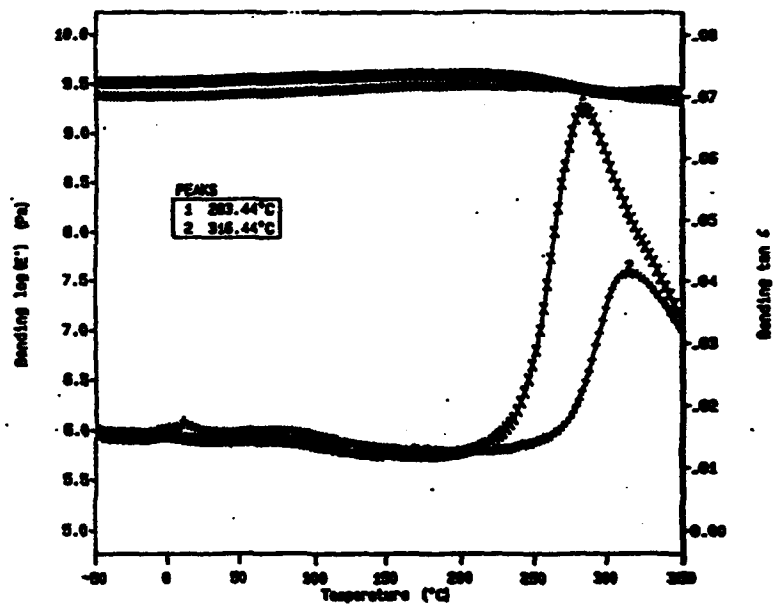


Figure 4. DMTA plot of Composites Laminates made from MAPS treated and untreated glass cloths.